



(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
21.07.1999 Bulletin 1999/29

(51) Int Cl.⁶: **C01B 3/36**, C07C 29/151,
C07C 41/00, C10G 2/00,
F25J 3/04

(21) Application number: 99300213.8

(22) Date of filing: 14.01.1999

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
 MC NL PT SE**
 Designated Extension States:
AL LT LV MK RO SI

(72) Inventors:

- Allam, Rodney John
Guildford, Surrey GU2 5EH (GB)
- Sheldon, Angela
Watton-on-Thames, Surrey KT12 1BB (GB)

(30) Priority: 20.01.1998 GB 9801200

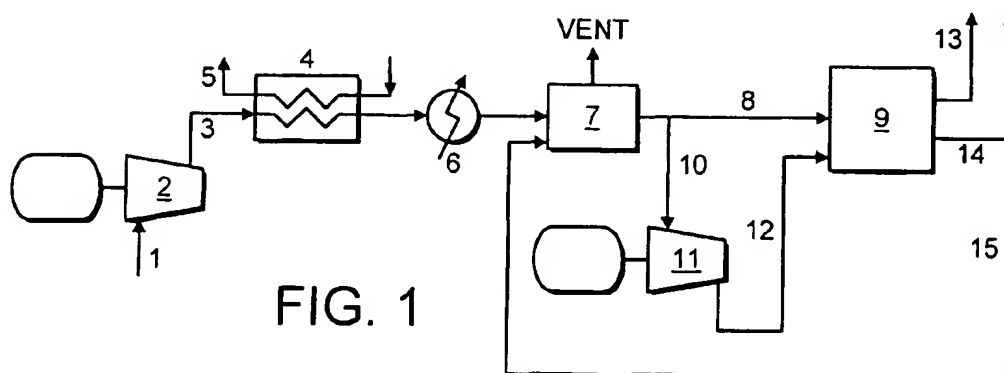
(74) Representative: **Burford, Anthony Frederick**
W.H. Beck, Greener & Co.
7 Stone Buildings
Lincoln's Inn
London WC2A 3SZ (GB)

(71) Applicant: **AIR PRODUCTS AND CHEMICALS, INC.**
Allentown, PA 18195-1501 (US)

(54) Integration of a cryogenic air separator with synthesis gas production and conversion

(57) The invention provides an improvement in the utilization of hydrocarbon feedstock by partial oxidation with oxygen to form a synthesis gas comprising carbon monoxide and hydrogen and subjecting the synthesis gas to a conversion process comprising an exothermic reaction. The oxygen is provided by air separation in which the feed air is at least partially compressed by work generated by expansion of a working fluid vaporized by indirect heat exchange with at least one of the

synthesis gas and the exothermic reaction. The improvement is that the working fluid is preheated by indirect heat exchange with adiabatically compressed feed air, thereby improving the overall efficiency of the process and reducing capital costs compared with conventional generally isothermal feed air compression. Preferably, the gas conversion process is a catalytic hydrogenation to prepare paraffinic hydrocarbons (Fischer-Tropsch reaction), methanol or dimethylether.



Description

[0001] The present invention relates to the integration of elevated pressure air separation with the production of a synthesis gas containing hydrogen and carbon monoxide (CO) from a hydrocarbon feedstock using oxygen obtained by air separation and subsequent use of the synthesis gas by an exothermic conversion process. It has particular, but not exclusive, application to the partial oxidation of natural gas and the conversion of the resultant synthesis gas to a liquid product by a catalytic hydrogenation process. The term "partial oxidation" used in this Application in respect of natural gas or other hydrocarbon feedstock means any reaction of the feedstock to produce synthesis gas which involves the use of oxygen even if conducted in the presence of steam or other reactive component unless it is clear from the context that only reaction with oxygen is intended.

[0002] Natural gas is often produced, either in association with crude oil or on its own, in a remote location where it is not economic to transport the gas to use points with pipelines. One method of recovering this gas is to convert it to paraffinic hydrocarbons or their oxygenated derivatives by catalytic hydrogenation. The term "catalytic hydrogenation" is used in this Application to mean contacting the gas with a catalyst whereby carbon monoxide in the gas is hydrogenated by the hydrogen content of the gas to produce paraffinic hydrocarbons or oxygenated derivatives, especially methanol and dimethylether but also aldehydes and ketones. The term "Fischer-Tropsch process" means such catalytic hydrogenation to prepare paraffinic hydrocarbons. Other uses of synthesis gas include the preparation of ammonia. These gas conversion processes are exothermic and conventionally the heat of reaction is used to generate steam.

[0003] The conversion of natural gas (or other hydrocarbon feedstock) to synthesis gas is accomplished using one of several standard methods available such as steam reforming, autothermal reforming, combined steam and autothermal reforming, combined reforming with pre-reforming partial oxidation and gas heated reforming etc. The most favourable systems to minimise overall equipment size and cost of production use processes in which oxygen is separated from air and used in, for example, an autothermal, combined reformer or partial oxidation system. The use of oxygen allows the production of synthesis gas having the high CO:H₂ ratio (1:1.6 to 1:2.5) required for a catalytic hydrogenation process without excess hydrogen production.

[0004] GB-A-2237287 discloses a methanol synthesis in which the feedstock is provided by reformed natural gas. The reforming is conducted with oxygen-enriched air and part of the reformed gas is subjected to a carbon monoxide shift reaction and the hydrogen content of the resultant gas stream mixed with the remainder of the reformed gas to provide a hydrogen-enriched feedstock for the methanol synthesis.

[0005] EP-A-0634562 discloses an integrated air separation-gas turbine power generation process in which synthesis gas is combusted with saturated, compressed gas turbine feed air to provide a combustion gas which is work expanded in the gas turbine to drive gas turbine feed air compressor(s) and provide power. The synthesis gas is prepared by reaction of a carbonaceous fuel with compressed air separation unit ("ASU") oxygen product. At least part of the ASU feed air is provided from a gas turbine compressor. The water used to saturate the compressed gas turbine feed air prior to combustion is heated using the heat of compression of the ASU oxygen product prior to synthesis gas production.

[0006] US-A-4,888,131 (Goetsch *et al*) and US-A-5,160,456 (Lahn *et al*) both describe the partial oxidation of natural gas with oxygen to produce synthesis gas and the conversion of that gas into liquid products by a Fischer-Tropsch process ("remote gas process") but do not describe the ASU used. Further information on the remote gas process is provided in a paper by Ansell *et al* ("Liquid/fuels from Natural Gas - An Update of the Exxon Process") presented at the Council on Alternate Fuels, Apr. 26-28, 1994 but again there are no details of the ASU.

[0007] A paper by Tijm *et al* ("Shell Middle Distillate Synthesis The Process, The Products, The Plant") presented at the Council on Alternate Fuels, Apr. 26-29, 1994 gives a summary of the remote gas process developed by Shell, but does not provide any details of the ASU.

[0008] A paper by Choi *et al* ("Design/Economics of a natural gas based Fischer-Tropsch plant") presented at the AIChE 1997 Spring National Meeting March 9-13, 1997 gives further economic and design information of a remote gas process but no information on the ASU.

[0009] WO-A-97/12118 (PCT/NO96/00227) has a detailed process description of, and provides heat and material balances for, a remote gas process but again fails to provide ASU details.

[0010] US-A-5635541 (Smith *et al*) describes a remote gas process in which part of the steam generated by the gas conversion reaction is used to drive the gas compression requirements of an elevated pressure ASU.

[0011] Conventionally, the air feed for an ASU is compressed in a generally isothermal manner using a multistage compressor with intercoolers. Little, if any, useful energy can be recovered from the intercoolers. However, US-A-4,461,154 (Allam) teaches that, at a sufficiently high compression ratio (at least 2.5:1), generally adiabatic compression of a gas produces a temperature sufficiently high to provide high grade energy which can be used directly or indirectly to assist in driving the compressor. The energy produced compensates for the additional power required for the adiabatic compression.

[0012] In particular, US-A-4,461,154 describes an air compression system having a steam turbine drive in which the

air is compressed adiabatically; the compressed air leaving the compressor is passed through an aftercooler where it heats boiler feedwater; the heated boiler feedwater is vaporized in the boiler producing superheated steam; and the steam used to drive the air compressor. The preheating of the boiler feedwater allows the excess heat in the boiler flue gas to be used for preheating air fed to the boiler for fuel combustion. The arrangement allows a substantial reduction in the fuel consumption for steam production. Further, the weight, volume, cost, footprint, and height of an adiabatic compressor are all considerably smaller than for a multistage compressor with intercoolers as used in conventional ASUs.

[0013] It is an object of this invention to integrate an ASU with synthesis gas production and conversion in a cost effective manner suitable for remote gas processing. It is a further object of the invention to integrate air separation and natural gas utilization for ease of installation on an offshore gas or gas/oil production platform or floating production storage and offloading system (FPSO). Other objects are to minimise the volume and weight of the ASU; to minimise the cost of the total facility power system by optimising the backup power supply required for start-up and operation of the ASU; and to more efficiently utilise the excess energy (usually in the form of steam) available from the gas conversion. Some or all of these objectives are achieved in varying degrees by processes of the present invention. Although the invention has been developed to meet these objectives, it is not limited to application in remote locations or to the use of natural gas but is of general application where appropriate conditions and requirements exist.

[0014] In a first aspect, the present invention is an improvement in a process for the utilization of a hydrocarbon feedstock in which the feedstock is partially oxidized using oxygen provided by air separation to form a synthesis gas comprising carbon monoxide and hydrogen and the synthesis gas is subjected to a conversion process comprising an exothermic reaction, and wherein the feed air for the air separation is at least partially compressed by work generated by expansion of a working fluid vaporized by indirect heat exchange with at least one of the synthesis gas and the exothermic reaction. The improvement consists in compressing the feed air in an adiabatic manner to provide preheat to the working fluid by indirect heat exchange with the compressed air.

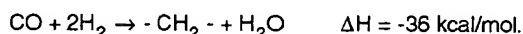
[0015] Optionally other plant gas compressors can be generally adiabatic compressors to supplement the preheat provided by the feed air compressor.

[0016] In another aspect, the invention is a corresponding improvement in the apparatus used for the feedstock utilization. This improvement is the provision of an adiabatic feed air compressor to provide heated air for preheating the working fluid, a heat exchanger for indirect heat exchange between the adiabatically compressed feed air and the working fluid to preheat the working fluid, and conduit means for conveying said preheated working fluid to vaporization means vaporizing the working fluid by heat exchange against the synthesis gas or exothermic reaction.

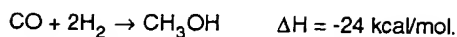
[0017] According to the present invention, there is provided an improvement in a process for the utilization of a hydrocarbon feedstock by partially oxidizing the feedstock with oxygen to form a synthesis gas comprising carbon monoxide and hydrogen and subjecting the synthesis gas to a conversion process comprising an exothermic reaction, said oxygen being provided by air separation in which the feed air is at least partially compressed by work generated by expansion of a working fluid vaporized by indirect heat exchange with at least one of the synthesis gas and the exothermic reaction, the improvement consisting in that the working fluid is preheated by indirect heat exchange with adiabatically compressed feed air.

[0018] The present invention also provides an improvement in an apparatus for the utilization of a hydrocarbon feedstock comprising a feedstock reactor for partially oxidizing the feedstock with oxygen to form a synthesis gas comprising carbon monoxide and hydrogen; a synthesis gas conversion reactor for subjecting the synthesis gas to a conversion process comprising an exothermic reaction; an air separation unit for separation of air to supply oxygen to the feedstock reactor and including a feed air compressor; a working fluid circuit including vaporization means for vaporizing the working fluid by indirect heat exchange with at least one of the synthesis gas and the exothermic reaction and an expander for producing work by expansion of the vaporized working fluid; and means coupling said expander to the feed air compressor whereby the feed air is at least partially compressed by work generated by the expander, the improvement consisting in that the feed air compressor is an adiabatic compressor providing heated air for preheating the working fluid and the working fluid circuit includes a heat exchanger for indirect heat exchange between the adiabatically compressed feed air and the working fluid to preheat the working fluid and conduit means for conveying said preheated working fluid to said vaporization means.

[0019] When the synthesis gas conversion process is a Fischer-Tropsch reaction, a large amount of heat is generated. The reaction can be represented as:



[0020] Less but still significant heat is generated when the process is a catalytic hydrogenation producing methanol and this reaction can be represented as:



[0021] Other exothermic synthesis gas conversion processes include the production of dimethylether from methanol formed *in situ* from the synthesis gas and the production of ammonia in which the exothermic reaction is the reaction of the hydrogen content of synthesis gas with nitrogen, which can be provided by the air separation process.

[0022] The synthesis gas conversion reactors usually are operated under generally isothermal conditions with the heat of reaction being removed by generating steam from heat exchange tubes within the reactor. The synthesis gas feed is produced in a high temperature reactor system utilising oxygen such as a partial oxidation reactor or an auto-thermal reforming reactor. The high temperature synthesis gas leaving the reactor needs to be cooled to the operating temperature of the gas conversion reactor, which is typically 220 to 280°C when preparing paraffinic hydrocarbons. The heat removed by said cooling could be used to generate high pressure steam for shaft power production. However, the gas conversion exothermic reaction is characterised by the liberation of all the heat at or above the temperature of the reaction and there is not enough heat available below this temperature level in the conventional process to provide all the low level heat required for feedwater preheating to supply the steam system. Use of an adiabatic feed air compressor in accordance with the present invention provides heat at a high enough temperature level to supply at least part of the feedwater preheating duty.

[0023] There are several advantages in using an adiabatic feed air compressor. Since it has no intercoolers, it is compact, relatively low in weight, has a small height and a small footprint compared to an intercooled compressor. There is no need for large cooling water flows to the compressor; usually a single trim cooler will be provided following the feed air/working fluid heat exchanger. These features make it easy to modularise the compression system and they are particularly desirable for offshore gas processing systems such as fixed platforms or an FPSO. The adiabatic compressors usually would be driven either by steam turbines or by electric motors with electricity generated from a steam turbine system with additional gas turbine backup.

[0024] Usually, the air separation will be cryogenic air separation but other elevated pressure air separation processes, especially pressure swing adsorption, can be used.

[0025] The feedstock usually will be natural gas but any other hydrocarbon feedstock conventionally used as a source of synthesis gas can be used.

[0026] The partial oxidation can be conducted by any of the known processes for producing synthesis gas which use oxygen but preferably is a process producing a gas having a carbon monoxide: hydrogen mole ratio of from 1:1.6 to 1:2.5.

[0027] Usually, the working fluid will be water.

[0028] The working fluid can be vaporized by indirect heat exchange with the synthesis gas and/or with the exothermic reaction. Usually, a first vaporized working fluid stream at a first pressure, for example 10 to 30 bara (1 to 3 MPa), provided by indirect heat exchange with the exothermic reaction and a second vaporized working fluid stream at a higher pressure, for example about 60 bara (6 MPa) is provided by indirect heat exchange with the synthesis gas and both vaporized working fluid streams are expanded to contribute to air compression requirement work.

[0029] The liquid working fluid preheated by indirect heat exchange with the adiabatically compressed air is supplied to the exothermic reaction heat exchange and/or to the synthesis gas heat exchange but usually will be supplied to the exothermic reaction heat exchange.

[0030] The following is a description, by way of example only and with reference to the accompanying drawings, of presently preferred embodiments of the present invention. In the drawings:

Figure 1 is a schematic representation of an air separation process for incorporation in a process in accordance with the present invention;

Figure 2 is a schematic representation of an integrated synthesis gas production and Fischer-Tropsch process for incorporation with the air separation process of Figure 1; and

Figure 3 is a schematic representation of an integrated synthesis gas production and methanol production for incorporation with the air separation process of Figure 1.

[0031] Referring first to Figure 1, a cryogenic air separation system comprises an axial flow adiabatic compressor 2 which compresses feed air 1 from ambient pressure to 5.5 bara. (0.55 MPa) and thereby raises its temperature from 20°C to 240°C. The compressed air 3 is cooled in an aftercooler 4 against 28 bar (2.8 MPa) feedwater to provide a preheated feedwater stream 5 at 230°C. The thus cooled feed air is further cooled to 20°C in a trim cooler 6 before entering an air purification absorber 7. Dry purified air leaving the absorber is split into a first substream 8, which is fed directly to a cryogenic air separator 9, and a second substream 10, which is further compressed to 60 bar (6 MPa)

in an intercooled multistage centrifugal compressor 11 before also being fed 12 to the separator 9. The feed air sub-streams 8,12 are separated in separator 9 by cryogenic distillation using a conventional pumped oxygen cycle to provide oxygen 13 at 40 bar (4 MPa) and waste nitrogen 14, a substream 15 of which is used for regeneration of absorber 7. Optionally the booster compressor 11 could be an adiabatic compressor with an aftercooler heating feed-water followed by a trim cooler.

[0032] The compressor 2 is driven via an electric generator/motor by a steam turbine 41 powered by steam generated in a gas conversion process (see Figure 2). Oxygen 17 at 40 bar (4 MPa) and 20°C supplied from the air separator 9 enters via line 17 and is preheated to 270°C against condensing 60 bar (6 MPa) steam in heat exchanger 18. Natural gas at 40 bar (4 MPa) is preheated to 270°C in heat exchanger 19 and fed 20, with the hot oxygen 21 and steam 22, into the burner of a partial oxidation reactor 23. The proportion of steam, oxygen and natural gas are such that the synthesis gas 24 produced has a hydrogen : carbon monoxide ratio of 2.14:1.

[0033] The synthesis gas 24 leaves the reactor 23 at 1083°C and is cooled in a waste heat boiler 25 to generate 60 bar (6 MPa) steam which is then superheated to 430°C in a synthesis gas cooler 26 to provide high pressure steam 16 for the turbine 41, reactor 23 and heat exchanger 18. The synthesis gas 27 leaving the cooler 26 is at 290°C and is divided into two substreams which are cooled in heat exchanger 19 and parallel heat exchanger 28, which superheats steam from a synthesis gas conversion slurry reactor 32 to provide 28 bar (2.8 MPa) steam 29 at 270°C. The synthesis gas is then further cooled to 40°C in heat exchanger 30 in which 60 bar (6 MPa) feedwater is preheated. Water is separated from the synthesis gas in the separator 31 and the residual synthesis gas 33 enters the slurry reactor 32 for Fischer-Tropsch conversion into paraffinic hydrocarbons. The heat generated in the reactor 32 is removed by evaporating water at 28 bar (2.8 MPa) which maintains the reactor temperature at 250°C. Saturated steam is produced from a steam drum 34 to supply the heat exchanger 28. Clean reactor effluent 35 is cooled to 150°C in a heat exchanger 36 to preheat feedwater at 28 bar (2.8 MPa) and the residual gas is separated from paraffinic hydrocarbon liquid product in a separator 37. The gas 38 provides fuel to a gas turbine power generation system (not shown) and the separated liquid product is cooled close to ambient temperature against cooling water in a heat exchanger 39. The cooled liquid is fed to a decanter vessel 40 where paraffinic hydrocarbons are separated from water.

[0034] 60 Bar (6 MPa) steam from cooler 26 and 28 bar (2.8 MPa) steam 29 are expanded in steam turbine 41, which is coupled to an electric generator/motor which also drives the main ASU air compressor 2. The system can be started by driving the electric motor and main air compressor using electric power supplied by a gas turbine using the fuel gas 38.

[0035] The 28 bar (2.8 MPa) feedwater requirement 42 of the system is provided by preheated feedwater 5 from the aftercooler 4 and preheated feedwater from heat exchanger 36 and the 60 bar (6 MPa) feedwater requirement 43 is provided by the preheated feedwater from the heat exchanger 30. If required, the preheated feedwater 5 could be at 60 bar (6 MPa) and used to supplement the preheated 60 bar feedwater from heat exchanger 30 instead of the preheated 28 bar (2.8) feedwater from heat exchanger 36. In a further alternative, heat exchanger 4 could heat two feed-water streams, one at 60 bar (6 MPa) and the other at 28 bar (2.8 MPa), to supplement preheated feedwater from both of the heat exchangers 30,36.

[0036] The exhaust steam is recycled to the system in conventional manner after condensation and deaeration.

[0037] Table I gives a summary of the main operating conditions for the process of Figures 1 and 2 without feedwater preheating by the adiabatic air compressor 2.

Table I

Stream No.	20	21	22	24	27	33	35	38	Oil/Max	16	29
Mole Fraction											
O ₂	0	0.9950	0	0	0	0	0	0	0	0	0
N ₂	0.0052	0.0050	0	0.0021	0.0021	0.0028	0.0034	0.0082	2.373E-04	0	0
CH ₄	0.8608	0	0	0.0079	0.0079	0.0102	0.0442	0.0675	0.0018	0	0
CO	0	0	0	0.2268	0.2268	0.2926	0.0661	0.1316	0.0025	0	0
H ₂	0	0	0	0.4854	0.4854	0.6261	0.2129	0.3254	0.0059	0	0
CO ₂	0.0161	0	0	0.0509	0.0509	0.0655	0.1351	0.2057	0.0162	0	0
H ₂ O	0	0	1	0.2269	0.2269	0.0030	0.4808	0.2469	0.0130	1	1
C ₂ H ₆	0.0802	0	0	0	0	0	0.0022	0.0034	1.489E-04	0	0
C ₃ H ₈	0.0266	0	0	0	0	0	0.0022	0.0034	1.451E-04	0	0
C ₄ H ₁₀	0.0057	0	0	0	0	0	0.0022	0.0034	1.716E-04	0	0
i-C ₄ H ₁₀	0.0029	0	0	0	0	0	0	0	0	0	0
C ₃ H ₁₂	9.0E-04	0	0	0	0	0	0.0022	0.0033	1.404E-04	0	0
iC ₅ H ₁₂	0.0010	0	0	0	0	0	0	0	0	0	0
C ₆ H ₁₄	5.0E-04	0	0	0	0	0	0	0	0	0	0
C ₇ H ₁₆	1.0E-04	0	0	0	0	0	0	0	0	0	0
C ₈ H ₁₈ (Average)	0	0	0	0	0	0	0.0267	0.0011	0.9597	0	0
Total Flow kmol/h	1863.51	1302.98	1568.68	7599.48	7599.48	5890.62	3000.64	1961.85	81.13	5980.00	6194.00
Temperature °C	270.00	270.00	250.21	1083.86	290.00	40.00	250.00	150.00	92.96	430.00	270.00
Pressure bara	40	40	40	40	28	28	28	28	28	60	28
Pressure MPa	4.0	4.0	4.0	4.0	2.8	2.8	2.8	2.8	2.8	6.0	2.8

[0038] Table II shows the quantity of 60 bar (6 MPa) and 28 bar (2.8 MPa) steam produced and the required feedwater preheat duty compared with the total available from heat exchangers 30 and 36. The deficiency is 21.69 MW. The duty available from the ASU main air compressor aftercooler 4 is 10.2 MW. Optionally, the use of an adiabatic booster compressor 11 can provide a further 4.8 MW.

TABLE II

<u>Steam Produced:</u>	60 bar (6 MPa) steam	29.9 kg/s
	28 bar (2.8 MPa) steam	30.97 kg/s
<u>Preheat Required:</u>	60 bar (6 MPa) steam	35.39 MW
	28 bar (2.8 MPa) steam	<u>27.87 MW</u>
	Total required	63.26 MW
<u>Preheat Available:</u>	Heat exchanger 30	27.61 MW
	Heat exchanger 36	<u>13.96 MW</u>
	Total available	41.57 MW
Preheat Deficiency		21.69 MW

[0039] Figure 3 shows a gas conversion process similar to that of Figure 2 but in which the synthesis gas is converted into methanol. The same reference numerals are used for corresponding items and only the main differences between the two processes are described.

[0040] The synthesis gas leaving the partial oxidation reactor 23 in line 24 is at 1091°C and, after cooling in the heat exchangers 25, 26, 19, 28 & 30 and passage through the separator 31, is compressed to 70 bar (7 MPa) in a compressor 59 and mixed with a recycle stream 60. The combined stream is preheated to 240°C in a heat exchanger 61 before it enters the methanol reactor system 32 via line 62. The heat generated in the methanol reactor 32 is removed by evaporating water at 28 bar (2.8 MPa) which maintains the reactor temperature at 250°C. Saturated steam is produced from the steam drum 34. The clean reactor effluent in line 65 is used in the heat exchanger 61 to preheat the synthesis gas entering the methanol reactor. The effluent stream is then cooled to 38°C in heat exchanger 36 and the methanol stream separated from the residual gas in line 38 in separator 37. A portion of this residual gas is recompressed to 70 bar (7 MPa) in a compressor 69 and recycled to the process via line 60.

[0041] Table III gives a summary of the main operating conditions for the process of Figure 3.

Table III

Stream No.	20	21	22	24	16	27	29	33	60	62	65	Methanol	38
Mole Fraction													
O ₂	0	0.9950	0	0	0	0	0	0	0	0	0	0	0
N ₂	0.0052	0.0050	0	0.0022	0	0.0022	0	0.0028	0.0122	0.0075	0.0100	2.912E-04	0.0122
CH ₄	0.8608	0	0	0.0076	0	0.0076	0	0.0098	0.0418	0.0259	0.0345	0.0020	0.0418
CO	0	0	0	0.2320	0	0.2320	0	0.2967	0.2423	0.2693	0.1987	0.0056	0.2423
H ₂	0	0	0	0.4896	0	0.4896	0	0.6261	0.5265	0.5758	0.4306	0.0056	0.5265
CO ₂	0.0161	0	0	0.0491	0	0.0491	0	0.0626	0.1696	0.1166	0.1495	0.0605	0.1696
H ₂ O	0	0	1	0.2194	1	0.2194	1	0.0022	9.906E-05	0.0011	0.0070	0.0375	9.906E-05
C ₂ H ₆	0.0802	0	0	0	0	0	0	0	0	0	0	0	0
C ₃ H ₈	0.0266	0	0	0	0	0	0	0	0	0	0	0	0
C ₄ H ₁₀	0.0057	0	0	0	0	0	0	0	0	0	0	0	0
i-C ₄ H ₁₀	0.0029	0	0	0	0	0	0	0	0	0	0	0	0
C ₅ H ₁₂	9.0E-04	0	0	0	0	0	0	0	0	0	0	0	0
i-C ₅ H ₁₂	0.0010	0	0	0	0	0	0	0	0	0	0	0	0
C ₆ H ₁₄	5.0E-04	0	0	0	0	0	0	0	0	0	0	0	0
C ₇ H ₁₆	1.0E-04	0	0	0	0	0	0	0	0	0	0	0	0
CH ₃ OH	0	0	0	0	0	0	0	0	0	0	0	0	0
Total Flow kmol/h	1864.10	1302.98	1479.58	7517.60	5966.00	7517.60	4394.00	5878.48	5990.45	11868.77	8927.70	1644.16	7283.54
Temperature °C	270.00	270.00	250.21	1091.45	430.00	290.00	270.00	40.00	43.84	240.00	250	37.83	37.83
Pressure bara	40	40	40	40	60	40	28	40	70	70	70	66	66
Pressure MPa	4.0	4.0	4.0	4.0	6.0	4.0	2.8	4.0	7.0	7.0	7.0	6.6	6.6

[0042] Table IV shows the quantity of 60 bar (6 MPa) and 28 bar (2.8 MPa) steam produced in the process of Figure 3 and the required feedwater preheat duty compared with the total available from heat exchangers 30 and 36. The deficiency is 10.71 MW. The duty available from the ASU main air compressor aftercooler 4 is 10.2 MW. Optionally, the use of an adiabatic booster compressor 11 can provide a further 4.8 MW.

TABLE IV

<u>Steam Produced:</u>	60 bar (6 MPa) steam	29.83 kg/s
	28 bar (2.8 MPa) steam	21.97 kg/s
<u>Preheat Required:</u>	60 bar (6 MPa) steam	35.32 MW
	28 bar (2.8 MPa) steam	<u>19.77 MW</u>
	Total required	55.09 MW
<u>Preheat Available:</u>	Heat exchanger 30	27.48 MW
	Heat exchanger 36	<u>16.90 MW</u>
	Total available	44.38 MW
Preheat Deficiency		10.71 MW

[0043] The use of adiabatic compression thus improves the overall efficiency of the processes of Figures 2 and 3, while at the same time, achieving the advantages of compactness, low weight, etc. mentioned previously, resulting in lower capital cost. The use of a steam power generation system allows for efficient utilisation of heat generated in the exothermic partial oxidation and synthesis gas conversion reactions. High temperature heat is retained for steam generation while adiabatic low temperature heat can be used for feedwater preheating.

[0044] It will be understood by those skilled in the art that the invention is not restricted to the specific details described above and that numerous modifications and variation can be made without departing from the scope of the following claims.

Claims

1. A process for the utilization of a hydrocarbon feedstock by partially oxidizing the feedstock with oxygen to form a synthesis gas comprising carbon monoxide and hydrogen and subjecting the synthesis gas to a conversion process comprising an exothermic reaction, said oxygen being provided by air separation in which the feed air is at least partially compressed by work generated by expansion of a working fluid vaporized by indirect heat exchange with at least one of the synthesis gas and the exothermic reaction, characterized in that the working fluid is preheated by indirect heat exchange with adiabatically compressed feed air.
2. A process as claimed in Claim 1, wherein said air separation is cryogenic air separation.
3. A process as claimed in Claim 1 of Claim 2, wherein said feedstock is natural gas.
4. A process as claimed in any one of the preceding claims, wherein said natural gas is in a remote location.
5. A process as claimed in any one of the preceding claims, wherein the exothermic reaction is a catalytic hydrogenation.
6. A process as claimed in Claim 5, wherein said catalytic hydrogenation is a Fischer-Tropsch synthesis producing paraffinic hydrocarbons.
7. A process as claimed in Claim 5, wherein said catalytic hydrogenation produces methanol.
8. A process as claimed in Claim 5, wherein said catalytic hydrogenation produces dimethylether.

9. A process as claimed in any one of the preceding claims, wherein the carbon monoxide: hydrogen mole ratio of the synthesis gas is from 1:1.6 to 1:2.5.
10. A process as claimed in any one of the preceding claims, wherein the working fluid is water.
11. A process as claimed in any one of the preceding claims, wherein the working fluid is vaporized by indirect heat exchange with the synthesis gas.
12. A process as claimed in any one of Claims 1 to 10, wherein the working fluid is vaporized by indirect heat exchange with the exothermic reaction.
13. A process as claimed in any one of the preceding claims, wherein a first vaporized working fluid stream at a first pressure is provided by indirect heat exchange with the exothermic reaction and a second vaporized working fluid stream at a higher pressure is provided by indirect heat exchange with the synthesis gas and both vaporized working fluid streams are expanded to contribute to air compression requirement work.
14. A process as claimed in Claim 13, wherein the exothermic reaction heat exchange is supplied with liquid working fluid at least partially preheated by indirect heat exchange with the adiabatically compressed air.
15. A process as claimed in Claim 13, wherein the synthesis gas heat exchange is supplied with liquid working fluid at least partially preheated by indirect heat exchange with the adiabatically compressed air.
16. An apparatus for the utilization of a hydrocarbon feedstock comprising a feedstock reactor for partially oxidizing the feedstock with oxygen to form a synthesis gas comprising carbon monoxide and hydrogen; a synthesis gas conversion reactor for subjecting the synthesis gas to a conversion process comprising an exothermic reaction; an air separation unit for separation of air to supply oxygen to the feedstock reactor and including a feed air compressor; a working fluid circuit including vaporization means for vaporizing the working fluid by indirect heat exchange with at least one of the synthesis gas and the exothermic reaction and an expander for producing work by expansion of the vaporized working fluid; and means coupling said expander to the feed air compressor whereby the feed air is at least partially compressed by work generated by the expander, characterized in that the feed air compressor is an adiabatic compressor providing heated air for preheating the working fluid and the working fluid circuit includes a heat exchanger for indirect heat exchange between the adiabatically compressed feed air and the working fluid to preheat the working fluid and conduit means for conveying said preheated working fluid to said vaporization means.
17. An apparatus as claimed in Claim 16 for conducting a process as claimed in any one of Claims 2 to 15.

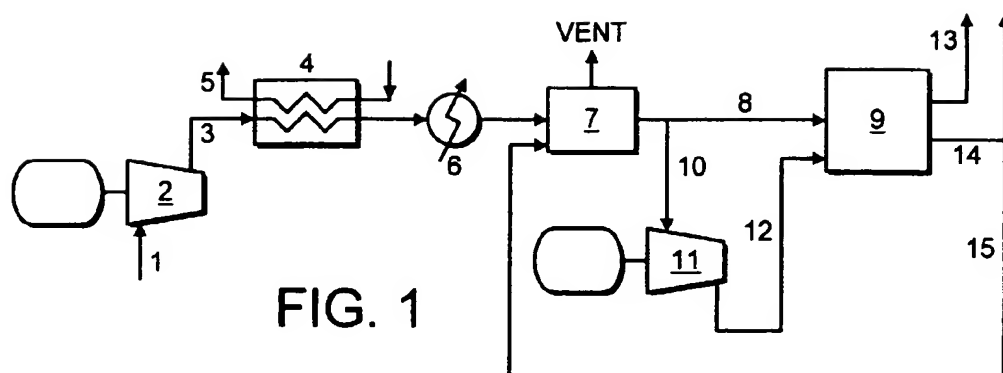


FIG. 1

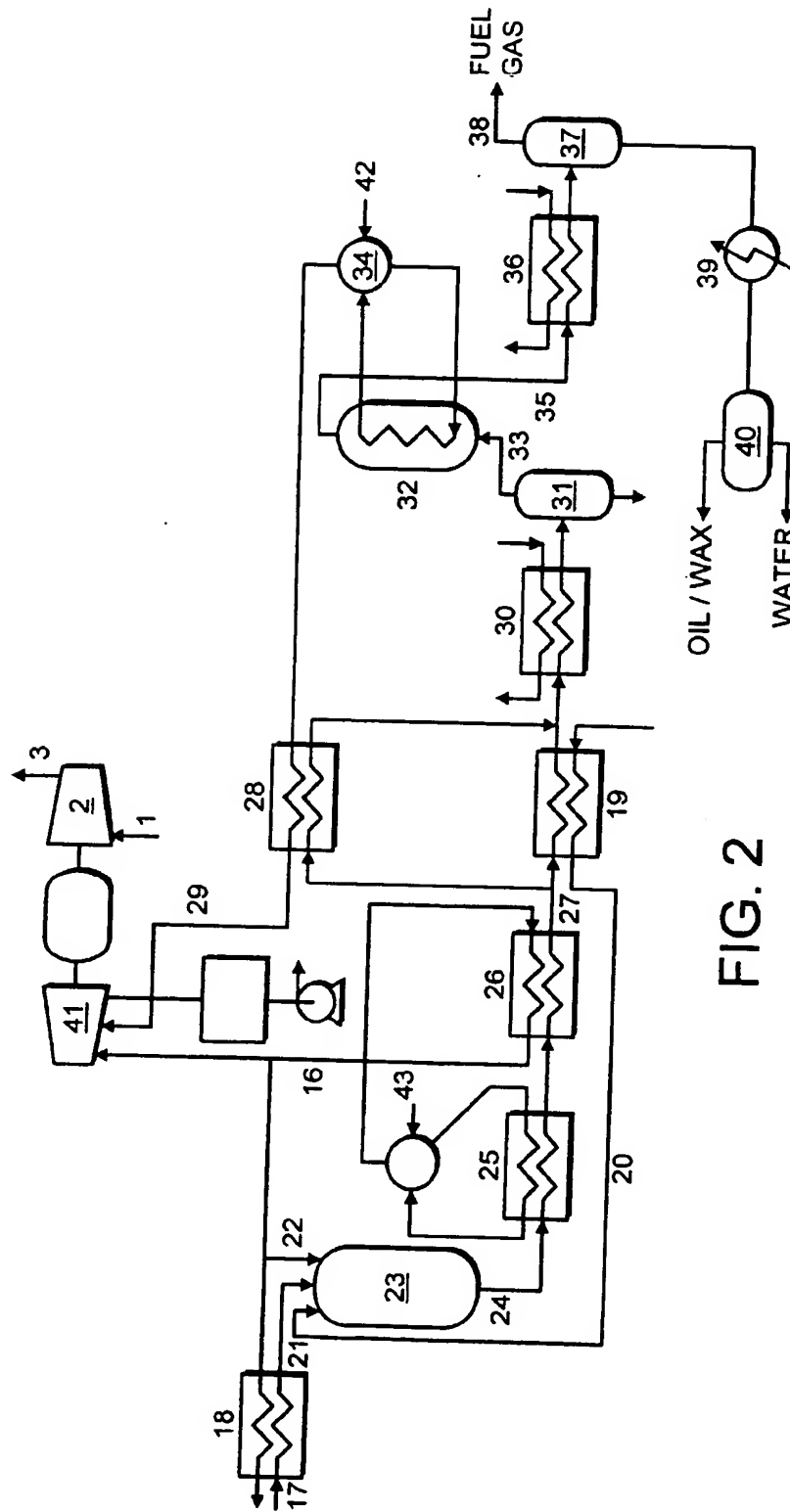


FIG. 2

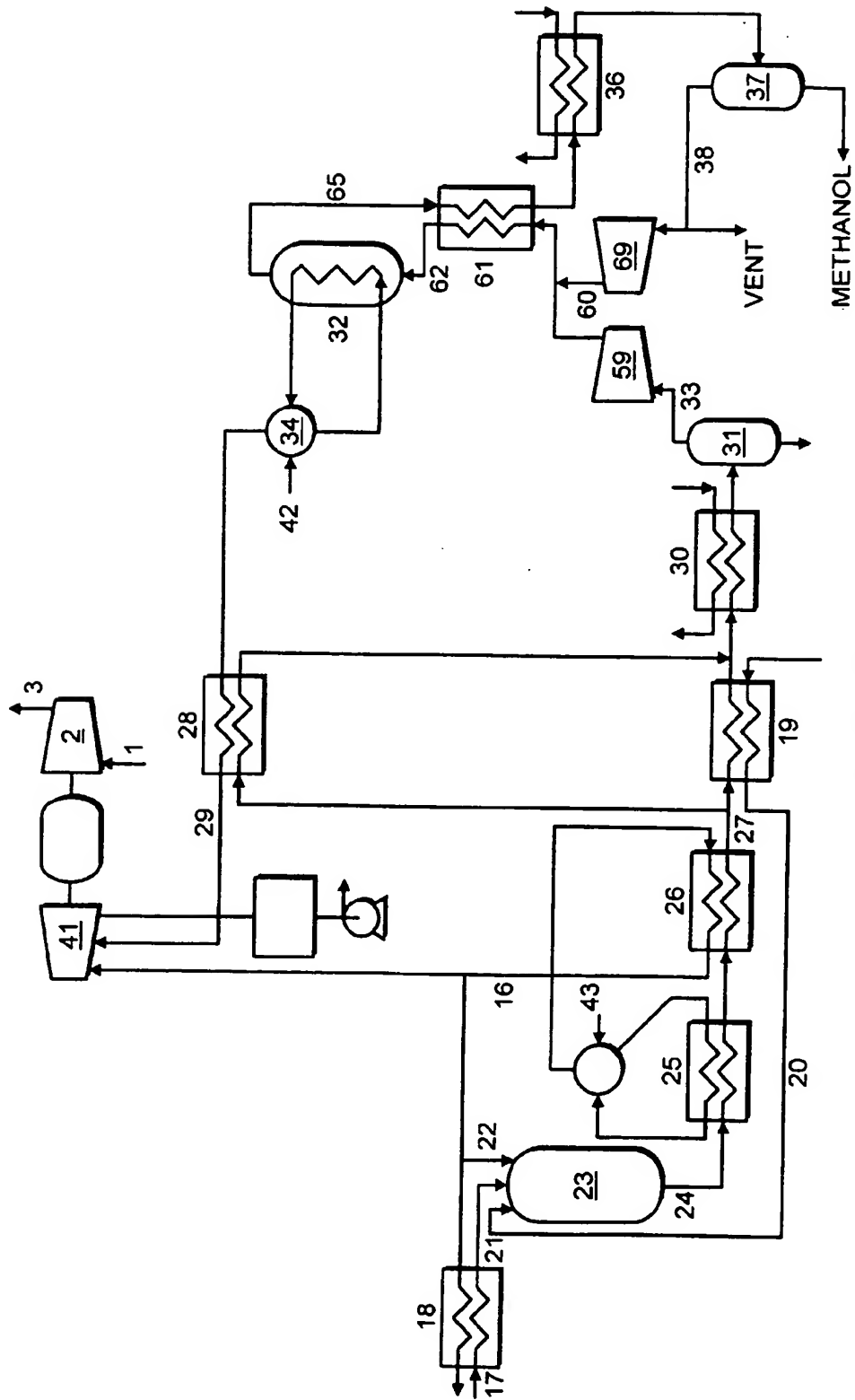


FIG. 3



(12) **EUROPEAN PATENT APPLICATION**

(88) Date of publication A3:
08.12.1999 Bulletin 1999/49

(51) Int Cl.⁶: **C01B 3/36**, C07C 29/151,
C07C 41/00, C10G 2/00,
F25J 3/04, C01B 3/38

(43) Date of publication A2:
21.07.1999 Bulletin 1999/29

(21) Application number: 99300213.8

(22) Date of filing: 14.01.1999

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
 Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 20.01.1998 GB 9801200

(71) Applicant: **AIR PRODUCTS AND CHEMICALS, INC.**
Allentown, PA 18195-1501 (US)

(72) Inventors:

- Allam, Rodney John
Guildford, Surrey GU2 5EH (GB)
- Sheldon, Angela
Walton-on-Thames, Surrey KT12 1BB (GB)

(74) Representative: **Burford, Anthony Frederick**
W.H. Beck, Greener & Co.
7 Stone Buildings
Lincoln's Inn
London WC2A 3SZ (GB)

(54) **Integration of a cryogenic air separator with synthesis gas production and conversion**

(57) The invention provides an improvement in the utilization of hydrocarbon feedstock by partial oxidation with oxygen to form a synthesis gas comprising carbon monoxide and hydrogen and subjecting the synthesis gas to a conversion process comprising an exothermic reaction. The oxygen is provided by air separation in which the feed air is at least partially compressed by work generated by expansion of a working fluid vaporized by indirect heat exchange with at least one of the

synthesis gas and the exothermic reaction. The improvement is that the working fluid is preheated by indirect heat exchange with adiabatically compressed feed air, thereby improving the overall efficiency of the process and reducing capital costs compared with conventional generally isothermal feed air compression. Preferably, the gas conversion process is a catalytic hydrogenation to prepare paraffinic hydrocarbons (Fischer-Tropsch reaction), methanol or dimethylether.

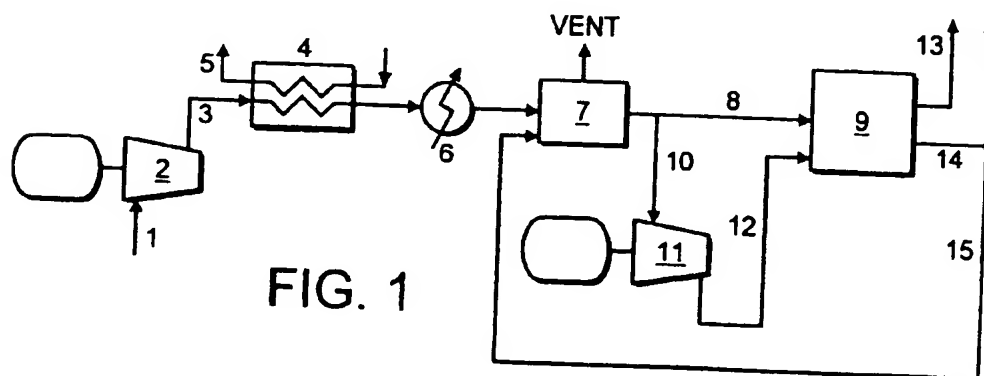


FIG. 1



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 30 0213

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US 3 962 300 A (HILLER HEINZ ET AL) 8 June 1976 (1976-06-08) * figure * * column 2, line 52 - column 3, line 28 * ---	1,7,10, 16	C01B3/36 C07C29/151 C07C41/00 C10G2/00 F25J3/04 C01B3/38
D,A	US 4 461 154 A (ALLAM RODNEY J) 24 July 1984 (1984-07-24) * the whole document * ---	1,10,16	
D,A	EP 0 748 763 A (AIR PROD & CHEM) 18 December 1996 (1996-12-18) * column 3, line 16 - line 33 * * claims * ---	1-6,16	
A	GB 2 179 056 A (HUMPHREYS & GLASGOW LTD) 25 February 1987 (1987-02-25) * the whole document * -----	1,16	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C01B F25J C07C C10G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19 October 1999	Examiner Van der Poel, W
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>			

EPO FORM 1500 03.92 (nov99)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 99 30 0213

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

19-10-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3962300 A	08-06-1976	CS 158698 B	25-11-1974
		DE 2024301 A	02-12-1971
		ES 389248 A	16-06-1973
		GB 1309872 A	14-03-1973
		JP 55050931 B	20-12-1980
US 4461154 A	24-07-1984	GB 2100801 A	06-01-1983
		AT 38539 T	15-11-1988
		AU 536757 B	24-05-1984
		AU 8494082 A	18-08-1983
		BR 8203563 A	14-06-1983
		CA 1210376 A	26-08-1986
		DE 3279208 A	15-12-1988
		DK 272882 A	19-12-1982
		EP 0069454 A	12-01-1983
		ES 513201 A	16-06-1983
		ES 513949 A	01-07-1983
		GR 76154 A	03-08-1984
		HK 17788 A	11-03-1988
		JP 58010526 A	21-01-1983
		PT 74992 A, B	01-07-1982
		ZA 8204288 A	27-04-1983
EP 0748763 A	18-12-1996	US 5635541 A	03-06-1997
		AU 676700 B	20-03-1997
		AU 5581396 A	02-01-1997
GB 2179056 A	25-02-1987	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82